



Short communication

Novel MoP/HY catalyst for the selective conversion of naphthalene to tetralin



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ARTICLE INFO

Article history:

Received 21 April 2014
Received in revised form 25 August 2014
Accepted 31 August 2014
Available online 17 September 2014

Keywords:

Coal tar
Naphthalene
MoP
Hydrogenation
Zeolite

ABSTRACT

MoP catalyst supported on HZSM-5, HBeta and HY were prepared by wet impregnation and temperature programmed reduction (H_2 -TPR), applied for the conversion of naphthalene to tetralin, and characterized by XRD, SEM, TEM, BET, H_2 -TPR, and NH_3 -TPD. Catalytic tests revealed the highest selectivity to tetralin was observed over MoP/HY with a naphthalene conversion of 85% and a tetralin selectivity of 99%. The effect of temperature and liquid hourly space velocity (LHSV) was also studied. Well dispersed and small particles of MoP, reduced pore size and weak acidity of HY contribute to enhanced catalytic activity and selectivity in conversion of naphthalene to tetralin.

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Introduction

Poly aromatic hydrocarbon compounds (PAH) in coal tar are the main feedstock for a large variety of essential chemicals and carbon-based materials. Naphthalene is the most abundant component of coal tar can be upgrade into useful product i.e., tetralin, a unique solvent in paint and pharmaceutical industries and an efficient hydrogen donor in fuel cells. It is also used as a constituent of motor fuels and lubricants; as a solvent for pesticides, rubber, asphalt, and aromatic hydrocarbons (HCs); as a dye solvent in the textile industry and as an intermediate in the production of agricultural chemicals such as carbaryl, napropamide, and 1-naphthoxyacetic acid [1–3]. Catalytic hydrogenation is the most effective route for converting low grade and complex HCs into useful chemicals [4,5]. The partial hydrogenation of naphthalene to tetralin is the main step in this reaction, so it requires bifunctional catalysts containing both active metals and acid sites that can operate at high hydrogen pressure and reaction temperature [6]. In this regards, the effect of metal catalyst on the hydrogenation of naphthalene has been investigated by a number of investigators. Some noble metal catalysts, including Rh, Ru, Ir, Pd

and Pt [7–14] are efficient candidate with high activity. However, the high cost and low abundance of these materials retard its commercial use. Transition metal catalysts such as Ni, Co, W metals supported on SiO_2 – Al_2O_3 , ZrO_2 , TiO_2 or activated carbon [15–20] are adopted for the hydrogenation of naphthalene; however the development of novel materials for the enhancement in tetralin selectivity are needed.

Recently a new group of transition metal phosphide catalysts have attracted increasing attention due to their high activity [21–29]. The overall activity of transition metal phosphide catalysts in the simultaneous hydrodesulphurization of dibenzothiophene, hydrodenitrogenation of quinoline and deoxygenation of ethanol was in the order of $Fe_2P < Co_2P < MoP < Ni_2P$ [26–29]. MoP possessed a moderate activity but its intrinsic property is six time higher than MoS_2 [30]. Therefore, it has the potential to function as efficient material in the selective hydrogenation of naphthalene. Zeolites, which encompass different pore sizes, acidities, and mechanical, chemical and hydrothermal stabilities, are useful support materials for hydrocarbon reactions [31,14]. Therefore, it was supposed that the properties of transition metal phosphides over zeolites can be tuned by regulating its metal dispersion, pore size and acidic properties for finding better carrier for the selective hydrogenation of naphthalene to tetralin. In this study, the activity and selectivity of molybdenum phosphides over zeolite supports in the hydrogenation reaction of naphthalene was evaluated. Based on several characterization techniques, the dispersion and diffusion of

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MoP over zeolite supports, as well as the catalyst pore size and acidity of zeolites were discussed to investigate the highly selective production of tetralin from naphthalene.

Experimental

The supports used in this study were HZSM-5, HBeta and HY. Supported MoP catalysts were prepared by wet impregnation and H₂-TPR as reported previously [26,28,30]. These catalysts were synthesized via two main steps. First, the solutions of the corresponding metal phosphate precursors were prepared by combining stoichiometric quantities of ammonium heptamolybdate $\{(NH_4)_6Mo_7O_{24} \cdot 4H_2O\}$ (Xilong, 99%), with ammonium phosphate $\{(NH_4)_2HPO_4\}$ (Xilong, 99%) in distilled water. These solutions were used to impregnate zeolite supports by wet impregnation method. The obtained samples were kept in an ultrasonic bath for 3 h and dried at 120 °C for not less than 6 h. After drying, the samples were calcined at 500 °C with a temperature ramp of 5 °C/min, grounded with a mortar and pestle, pelletized with a 10 MPa press (769YB-24B), and then sieved to particle sizes of 20/40 mesh.

In the second step, the resulting phosphates were reduced to phosphides in a U-shaped quartz reactor with a 100 cm³/min g hydrogenous flow (at 5 °C/min). The samples were kept for 3 h on their highest reduced temperatures. The highest reduction temperatures were 610 °C for MoP/HZSM-5, 560 °C for MoP/HBeta and 545 °C for MoP/HY. To save and protect the structure of the reduced catalyst by air exposer, passivation was done at room temperature in a 1% O₂/N₂ flow for 2 h. The total weight percent of the active MoP was kept 10% over all zeolite supports. The prepared catalysts were characterized by X-ray diffraction (XRD), temperature programmed reduction of hydrogen (H₂-TPR), N₂ adsorption, scanning electron microscope (SEM), transmission electron microscopy (TEM), Brunauer–Emmett–Teller (BET) and temperature-programmed desorption of ammonia (NH₃-TPD).

The hydrogenation of naphthalene was carried out using a fixed-bed reactor (i.d. = 1 cm) packed with 8 mL of catalysts in the isothermal section, sealed with 1 mm diameter glass beads at both ends. The reactor was operated at 300 °C and hydrogen pressure of 4.0 MPa using 10 wt.% naphthalene in *n*-heptane as model feed. The oxidic surface protective layer of passivated catalyst was removed and activated by H₂ flow of 30 L/h at 400 °C for 2 h. After cooling to the reaction temperature, 10 wt.% solution of naphthalene was pumped into the reactor, using a 2PB00 C (B Satellite Co.) metering pump, at 0.4 mL/min into a 36 L/h of H₂. Liquid products of the reaction were collected in a condenser placed at the reactor exit. The reactants and products were analyzed by GC–MS and were classified as naphthalene, tetralin and other products (i.e., decalin, alkylcyclohexanes, alkyl benzenes and alkyl indenenes). Periodic analysis of the gas phase effluents showed no significant quantities of low carbon products. The naphthalene conversion and tetralin selectivity were calculated based on the peak areas of the GC by considering the different sensitivity factors of the GC–MS detector. The naphthalene conversion and product selectivity for tetralin are defined in Eqs. (1) and (2), respectively:

$$\text{Naphthalene conversion (mol\%)} = 100 \times \frac{M C_{10}H_{8(\text{in})} - M C_{10}H_{8(\text{out})}}{M C_{10}H_{8(\text{in})}} \quad (1)$$

$$\text{Tetralin selectivity (mol\%)} = 100 \times \frac{M C_{10}H_{12}}{M C_{10}H_{8(\text{in})} - M C_{10}H_{8(\text{out})}} \quad (2)$$

where *M* represents molar concentration of inlet and outlet species, while C₁₀H₈ and C₁₀H₁₂ are the molecular formulas of naphthalene and tetralin respectively.

Results and discussion

Fig. 1 shows the phase and phase composition of the synthesized molybdenum phosphides by comparing peaks with standard powder diffraction patterns [32]. The diffraction pattern of zeolite supported MoP shows low intensity diffraction peaks at 2θ° 32.1°, and 43.14°, indicating the smaller particles and high dispersion of MoP over the zeolite supports. The dispersion of the metals over the zeolite supports increases from HZSM-5 to HBeta and HY. The particle sizes of the catalysts were calculated from XRD according to Scherrer equation and summarized in Table 1. The supported MoP catalyst appeared to have different particle size based on the supports. The MoP/HY had smallest particles, indicating better dispersion. Similar results observed in the previous study [33]. The MoP/HBeta has wider particle size than MoP/HY. On the other hand MoP/HZSM-5 gave highest particle size and lowest dispersion in the order: MoP/HY > MoP/HBeta > MoP/HZSM-5. Fig. 2 shows the surface morphology of the phosphide catalysts over zeolite supports, showed well-faceted crystal morphologies, consistent with the results reported by Bussell et al. [27].

Fig. 3 shows the H₂-TPR experiments of MoP over zeolite supports, reflect the reducibility of the active species which are closely related to the interaction between active metal species and the supports. The TPR of MoP shows two reduction peaks: the first is assigned to the Mo⁶⁺ reduction to Mo⁴⁺ [34] and the second is attributed to the overlapping of different peaks, corresponding to the reduction of Mo⁴⁺ to Mo⁰ on one hand and of P⁵⁺ to P⁰ on the other. Previously it was shown that some of the phosphide are lost during TPR (presumably as PH₃) [27,30,35] which reduce the pore size of the final catalyst. Among the three serial catalysts, HY zeolite show an easily reducible tendency better than those of HBeta and HZSM-5 (i.e., HY < HBeta < HZSM-5). These preparation conditions significantly affect the structure and acidity of the catalyst. It is found from the XRD results that MoP formed large particle size over HZSM-5 than HBeta and HY with a direct relation with highest reduction temperature. HZSM-5 having the highest reduction temperature formed high particle size while MoP over HY have the lowest particle size due to the lowest synthesis temperature. The smallest particle size of MoP over HY zeolite also confirmed from the TEM images as

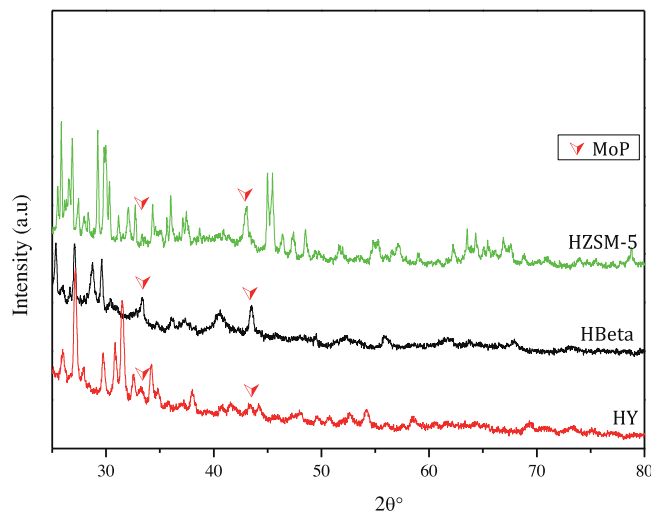


Fig. 1. XRD patterns of MoP over zeolites.

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